Study of the Growth Parameters Involved In
Synthesizing Boron Carbide Filaments

First Quarterly Report

by

A. Gatti
R. Cree
R. Mehan
C. Mancuso

September 1964

Prepared for National Aeronautics and
Space Administration

under Contract NASw 937

Space Sciences Laboratory
Missile and Space Division
General Electric Company
P. O. Box 8555, Philadelphia 1, Pa.

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I. SUMMARY

The present program is a continuation of a study sponsored by NASA on Contract NASw-670. The current program is concerned with (1) the synthesis of boron carbide whiskers, (2) the characterization of these whiskers in terms of their chemical and physical properties at room and elevated temperatures, and (3) the utilization of such whiskers in composites.

In addition to the routine runs which provided a supply of B_4C whiskers for further studies, considerable emphasis was placed on a search for an effective catalyst which would markedly increase both the quantity and the size of B_4C whiskers grown. It was found that vanadium serves as the best catalyst in this respect.

Since the surface perfection of the micro-crystals play an important role in the determining their strength, studies on surface morphology of B_4C whiskers was initiated.

Several tensile tests of the B_4C whiskers were performed previously at room temperature in order to determine their strengths and strength distribution. Thus far, from a total of twenty tests, tensile values varied from a low of 179,000 psi to a high of 965,000 psi with an average value of 400,000 psi. Plans for elevated temperature tests are underway and are discussed along with the problems to be solved.

Composites of B_4C-epoxy and B_4C-aluminum were fabricated and tested in tension at room temperature. Tensile values as high as 29,500 psi have been measured for the B_4C epoxy composites while values of 29,000 psi have been measured for B_4C-aluminum composites. Attempts to infiltrate B_4C whiskers with fernico "5" have not been successful thus far.

Future work will include further studies of the growth process, and a continuing materials characterization program. Basic tensile properties of individual B_4C whiskers at elevated temperatures will be measured. Elevated temperature tests of composites will be attempted and evaluated.

II. INTRODUCTION

In a previous study[1], whiskers of B_4C were synthesized for the first time so that their crystalline and mechanical properties could be determined. In addition, preliminary studies were undertaken for the purpose of evaluating composite materials containing B_4C whiskers. The results of this study have shown that B_4C crystals possess an excellent combination of physical properties, in terms of high elastic modulus, high strength, and low density. It is this combination of properties which hold the greatest potential for high strength-to-weight or high stiffness-to-weight materials of the future. In addition, the refractory properties of B_4C whiskers make them a prime candidate for reinforcing materials at high temperatures.

The present investigation is a continuation of this study, with special emphasis being placed on (1) the scale-up of B_4C whisker production, (2) the testing of individual whiskers at elevated temperatures, and on (3) the fabrication and testing of composites containing these whiskers.

Since the fabrication of B_4C composites is dependent on an adequate supply of high strength whiskers, any technique which can increase significantly the rate of whisker formation is worthy of investigation. Studies during this quarter have resulted in the discovery of an effective catalyst which appears to control the size and number of B_4C whiskers. Concurrent with continuing growth studies, an extensive appraisal of whisker surfaces has been started. A number of small B_4C composites fabricated with epoxy and aluminum matrices have been tested in tension at room temperature. These test results will be included in this progress report.

III. EXPERIMENTAL PROCEDURES AND RESULTS

A. GROWTH STUDIES

1. Description of Equipment

Growth studies during this period were performed in graphite resistance furnaces which have been described elsewhere[1]. No important changes in the furnances or auxiliary equipment have been necessary.

2. Growth of B_4C Whiskers

Three techniques were developed previously for growing B_4C whiskers, and these are described as follows: (a) The pure vapor method, in which a charge of powdered B_4C is heated in a "lazy Susan" type tray in order to enhance the vaporization of pure B_4C. Whiskers of B_4C are then formed in a cooler region of the furnace, (b) The dynamic method, which consists of controlling the flow of the individual gases which react to form B_4C as they flow through a smaller furnace containing two variable hot zones, and (c) A combination of methods (a) and (b) which utilizes a carrier gas flowing over a "lazy susan" charge of pure B_4C powders in the small two-zoned furnace.

The present growth studies have concentrated on routine runs to furnish whiskers for composite fabrication utilizing the pure vapor method and on the development of an effective catalyst which would control the size and population of B_4C whiskers. The latter work is important to B_4C growth technology since it offerss a means to significantly increase the supply of B_4C whiskers.

The effect of a catalytic impurity was suspected in the earlier growth studies, since it was observed that continued use of the same B_4C supply in the pure vapor method led to a decrease in the population and in the length of B_4C whiskers produced. Five or six reruns were sufficient to reduce growth to essentially zero. Indeed, various batches of B_4C powders were observed to produce notable differences in the length and in the number of whiskers grown. Semi-quantitative spectrographic* analysis were obtained of two lots

*Analyses were obtained from the W.B. Coleman Laboratories, Philadelphia, Pa.

of B_4C powder as received and after being used in furnace runs to produce whiskers. It was found that a large number of impurities were present before reaction, namely (in decreasing amounts): Fe, Al, Ca, Si, Cr, Ni, Cu, Mn, Ti, W, V and Mg. After whisker growth, Fe, Ti, Cu, and Si remained in detectable quantities. It was first thought that one or more of these elements remaining after reaction would be effective in promoting whisker growth, and further, that the gradual decrease in whisker population was a direct result of the decreasing concentration of one or more of these elements. Experiments were performed, therefore, in which the elements Fe, Ti, Cu and Si were added purposely* to exhausted B_4C charges which would no longer produce whiskers. No significant effects on the growth of B_4C whiskers were noted.

It was then decided to analyze the whiskers themselves by x-ray fluorescence. A trace amount of vanadium was detected in all whiskers analyzed. Hence, an experiment similar to that previously described was performed utilizing an exhausted charge of B_4C powder mixed with 1 wt. % vanadium metal powder. A standard run of $1950^{\circ}C$ for 5 hours was performed and the result was a rejuvenation of B_4C whisker growth from the formally exhausted powder. Additional experiments have since been performed to confirm this finding. The growth of whiskers obtained by the addition of V to exhausted B_4C powder is equal to the best whisker growths obtained with fresh powder. The effect of the vanadium addition can be clearly seen in Figure 1, where the upper tube shows no appreciable whisker growth from exhausted B_4C powder, while the lower tube shows a notable growth of whiskers after vanadium had been added to the charge.

The dynamic growth method, produced B_4C whiskers in situ from the gas phase according to the reaction: $4BCl_3 + CH_4 + 4H_2 \rightarrow B_4C + 12HCl$. This method yielded only poorly developed whiskers. The addition of vanadium to this system was also studied, and by heating BCl_3, CH_4 and H_2 to tem-

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*Fe, Ti, Cu, and Si were added in the elemental form, and in various combinations and propertions.

peratures of 1650°C for 5 hours, a band of well defined B_4C whiskers were produced in the furnace tube.

Conditions are not yet optimized and much experimentation remains. However, it is now possible to grow whiskers by this dynamic method and it is probable that with further experiments that this method will be capable of producing B_4C whiskers of better quality and population than the pure vapor method.

B. MECHANICAL PROPERTIES OF B_4C WHISKERS

1. Elevated Temperature Properties of B_4C Whiskers

Considering the relatively short length of B_4C whiskers available, direct tension tests at high temperatures do not appear feasible because of gripping difficulties. Consequently, high temperature strength data will be attempted by using the bend test method. The system to be used is shown schematically in Figure 2.

A platinum or tungsten wound furnace will be used to provide heat, and an inert gas will fill the system in order to protect the specimen and the furnace windings.

Although this scheme appears conceptually simple, several difficulties in obtaining accurate strength data are anticipated. Apart from the usual handling and aligning problems always present in whisker testing, two main areas of concern appear to be present:

a. Whisker Geometry - The ultimate bending stress is computed by the equation

$$S = \frac{Mc}{I}$$

where M = bending moment
c = distance from neutral axis to outer fiber
I = moment of inertia

Except for the light loads involved, there should be little difficulty in measuring M. However, both c and I are dependent on the geometry of the cross-section and its orientation. The orientation will be most difficult to determine, and hence the value of the bending strength will be correspondingly uncertain.

b. Effect of Plastic Flow - Conventional beam formulas are based on elastic behavior of materials. At higher temperatures, plastic flow is likely to occur in the whisker. To obtain ultimate strength values which will be related to the uniaxial strength, corrections for plasticity will have to be made. This will be somewhat difficult because of anisotropy and varying cross-sectional areas.

C. CRYSTAL AND MORPHOLOGICAL CHARACTER OF B_4C WHISKERS

It has been suggested that whisker type filaments derive their excellent mechanical properties from their lack of dislocations or lack of mobile dislocations and from their surface perfection.

The lack of dislocations, or at least dislocations which do not interact with applied stress (i.e., parallel to the stress axis), can be deduced by assuming that the crystal size limits the number of dislocations which could be accommodated while slow growth conditions at low supersaturation allow atomic arrangement to proceed without accident. Surface perfection arises from growth conditions which essentially limit the growth environment so that only enough material is available to increase the length of the growing crystals while not allowing additional nucleation to occur.

The orientation and growth habits of B_4C whiskers have been discussed in a previous report[1]. However, little emphasis has been placed on ascertaining their perfection. Such a study to clarify the state of perfection of B_4C whiskers is now underway. Work during this quarter has dealt with the surface optical smoothness utilizing light and electron microscopy. Earlier electron micrographs had shown that parallel overgrowths exist although the whiskers would appear smooth at low magnifications, however, since these initial results, improvements in growth procedures have increased the smooth variety of whiskers (i.e., whiskers of high perfection). Figures 3a and 3b are examples of highly perfect whiskers. It is estimated that 50% of the total whiskers grown per run are of the "good" variety, which is a marked improvement over the earlier growth results.

D. COMPOSITE STUDIES

Three matrix materials have been selected for utilization in the composite studies: (1) Fernico "5", (2) PJ 122 epoxy, and (3) Aluminum.

Fernico "5" represents a high temperature material and was selected on the basis of sessile drop results[1]. PJ 122 epoxy was chosen because of its ease of handling, tensile strength and wetting ability. Aluminum is extremely useful for structural applications where high strength-to-weight requirements at moderate temperatures are required.

1. Impregnation Techniques

The technique used was essentially that developed by Jakas for the formation of composites containing alumina whiskers[2]. A quartz tube is drawn into a capillary whose small diameter lies between 5 to 20 thousandths of an inch. B_4C whiskers are placed in the tube through a glass funnel attached to the top of the quartz tube-capillary and are vibrated or tapped into place. Care must be exercised when tapping the tube since the fine tip of the capillary portion is easily broken. Although such vibration permits better packing of the whiskers, thereby increasing the volume fraction of the resulting composite, failure in the capillary and subsequent loss of the whiskers is risked.

The whisker laden quartz tube-capillaries are subsequently used for all impregnating experiments using both resins and metals.

Resin impregnation is fairly simple. Figure 4 shows a typical arrangement comprised of a ring stand, a whisker laden tube-capillary and a disposable plastic syringe filled with PJ 122 fluid epoxy. Pressure is applied and the epoxy is allowed to flow into the whisker bundle. Curing the epoxy is accomplished by oven heating to $180^{\circ}F$ for 16 hours. The quartz sheath is removed by HF etching, and tensile grips are added to the composite by using a more viscous epoxy which will form a generous bead through surface tension action.

In the case of metal-composite specimens, wires of the matrix metal are also packed into the tube containing the whiskers. The tube is then joined to a long quartz tube, which is then placed in a vacuum apparatus, and the matrix metal is melted by an inductively heated tantalum susceptor. When molten, the metal is forced through the whisker bundle by inert gas pressure. The composite is directionally solidified from the bottom tip to its miniature riser by simultaneous decrease in power and withdrawal of the composite through the hot zone. Figure 5 is a schematic representation of the described apparatus first designed for the infiltration of alumina whisker composites under contract NOw 60-0465d for the Bureau of Naval Weapons[2].

2. Fernico "5" Composites

B_4C exhibits some metallic characteristics and can be wetted by some molten metals as well as being bonded to these metals upon solidification. Metals which wet B_4C, then, are a good choice for a matrix material with which to bind B_4C whiskers together in a composite. Previous work[1] has shown that Fernico "5" would be a good high temperature matrix, since it formed a contact angle of 30^{o} with B_4C which is indicative of good wetting.

The impregnation of B_4C whisker bundles of Fernico "5" has proved difficult however. Boron is readily dissolved by molten Fernico "5", necessitating the addition of boron to the composite to minimize molten metal attack of the whiskers during impregnation. This was accomplished by placing chunks of bulk B_4C in the tube below the Fernico "5" wire charge. Thus the molten Fernico "5" should trickle past the boron carbide chunks, reaching the solubility limit for boron before impregnating the B_4C whisker bundle. When this was attempted, the metal was located further up the tube than where it was originally placed, even though it had been obviously melted. It is postulated that gas evolution during the boron-Fernico "5" dissolution caused the resulting melt to be forced back up the tube and out of the hot zone. Attempts to minimize this action by mixing boron carbide in the wires has proved unsuccessful. Pre-alloying boron-Fernico "5" slugs under vacuum will be tried as a means of eliminating this problem.

3. PJ 122 Composites

PJ 122 composites had been made previously[1]. The highest tensile value reached was 24,700 psi for a 10 v/o whisker content and represented an average tensile value in the whiskers of 193,000 psi. These initial experiments were conducted using the available whiskers. If the yield of whiskers was low for a given run, the product of several runs would be combined in order to have a sufficient quantity of whiskers to make one composite test specimen.

During present work, considerable care was taken in selecting only long straight B_4C whiskers taken from several furnace runs. In one composite specimen (No. 60-SSL-9-56-p3), only whiskers ranging from 1/4 inch in length and upwards were used. Table I presents a compilation of tensile data at room temperature for this composite. A maximum stress of 29,500 psi was supported by the sample. The whisker volume fraction of this particular sample was 5% representing an average tensile load on the whiskers of 505,000 psi.

Thus far, it has been possible to produce composites containing a whisker packed density up to 10% by volume. Volume fractions of 30% or more will have to be achieved in order to produce ultra-high-strength composites.

4. Aluminum Composites

Aluminum-B_4C composites were fabricated without major difficulty. Whisker bundles were selected without descrimination as to size or shape, and bundles were impregnated with the liquid metal as previously described. The whiskers were readily wetted by the molten aluminum. There was some difficulty in flowing the molten metal completely through the whisker capillary due to the pressure drop across the bundle and the very small opening in the bottom of the capillary tube.

Table II presents a compilation of the room temperature tensile data of the aluminum-B_4C composites made to date. Samples for these tests were formed similarly to the epoxy based specimens (i.e., epoxy beads for grips, etc.)

TABLE I

TENSILE DATA OF B_4C - EPOXY SPECIMENS

Test Reference No.	Breaking Load (lbs)	Breaking Stress (psi)	Remarks
60-SSL-9-56-p1	4.4	8800	obvious defect (void)
60-SSL-9-56-p2	4.5	15,200	broke in grip
60-SSL-9-56-p3	6.7	29,500	broke in grip
60-SSL-9-56-p4	8.0	27,000	broke in grip

TABLE II

TENSILE DATA OF B_4C - ALUMINUM SPECIMENS

Test Reference No.	Breaking Load (lbs)	Breaking Stress (psi)	Remarks
60-SSL-9-56-A1	3.4	-----	Grip Pulled Out
60-SSL-9-56-A2	3.8	-----	Grip Pulled Out
60-SSL-9-56-A3	5.6	16,200	Broke in Grip
60-SSL-9-56-A4	5.8	29,000	Broke in Grip
60-SSL-9-56-A5	6.45	18,700	Broke in Grip
60-SSL-9-56-A6	4.25	14,400	Broke in Grip

Although this phase of the work is of a preliminary nature, the strength values indicate that reinforcement has been achieved. The maximum tensile value measured, 29,000 psi is well above the yield stress of pure aluminum. Figure 6 is a cross section of a typical aluminum-based composite.

IV. CONCLUSIONS

A significant contribution to the technology of growing B_4C whiskers was made. It was discovered that additions of vanadium to the whisker growing process would greatly enhance the yield and size of individual B_4C whiskers. Vanadium powder additions when added to exhausted B_4C powder (powder which would no longer grow whiskers) showed an equal or better growth of B_4C whiskers than the best B_4C bulk powders used to date in the pure vapor method. Vanadium chloride gas additions to the dynamic growth method were also successful. A patent disclosure has been written to document this discovery.

The strongest composite to date was an epoxy composite whose tensile strength was 29,500 psi. Since the tensile strength of the epoxy alone is 6,000 psi, an almost 5-fold increase in strength has been achieved. This composite contained only 5 v/o whiskers which corresponds to an average stress of 505,000 psi in the whiskers. The next strongest composite tested was aluminum based and withstood a tensile load of 29,000 psi. Since the yield stress of pure aluminum at room temperature is about 7,000 psi a four-fold increase in yield strength has been achieved. This composite contained 10 v/o B_4C whiskers which corresponds to an average stress in the whiskers of 236,000 psi.

Tensile tests conducted on composite specimens have resulted in significantly higher strengths than those tested previously. This is due primarily to better whisker selection and the elimination of debris.

However, in order to get higher strength composites more effort will have to be directed toward the following:

(1) Better whisker quality

(2) Higher volume fraction composite

(3) Better testing methods to minimize grip failure

V. FUTURE WORK

Future work will include continued studies of B_4C whisker growth parameters. Since geometric effects appear to also affect the growth density of the whiskers, studies will be directed toward the understanding and optimization of this parameter.

Attempts will be made to determine the mechanical properties of B_4C whiskers at elevated temperatures, and techniques will have to be developed for testing such small samples.

Structure studies will continue with the main emphasis being placed on a study of the degree of perfection of B_4C whiskers.

Composite studies will continue and expand. Improved techniques for fabricating, testing and evaluating composites are being developed and utilized. More emphasis will be placed on the aluminum-B_4C and Fernico-B_4C composites.

ACKNOWLEDGEMENTS

Acknowledgement is given to Messrs. W. Laskow, C. Miglionico and T. Harris for their valuable assistance in this program.

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2. Sutton, et al, "Development of Composite Structural Materials for High Temperature Applications," Quarterly Reports 1-17, Navy BuWeps (Contract NOw 60-0465d).

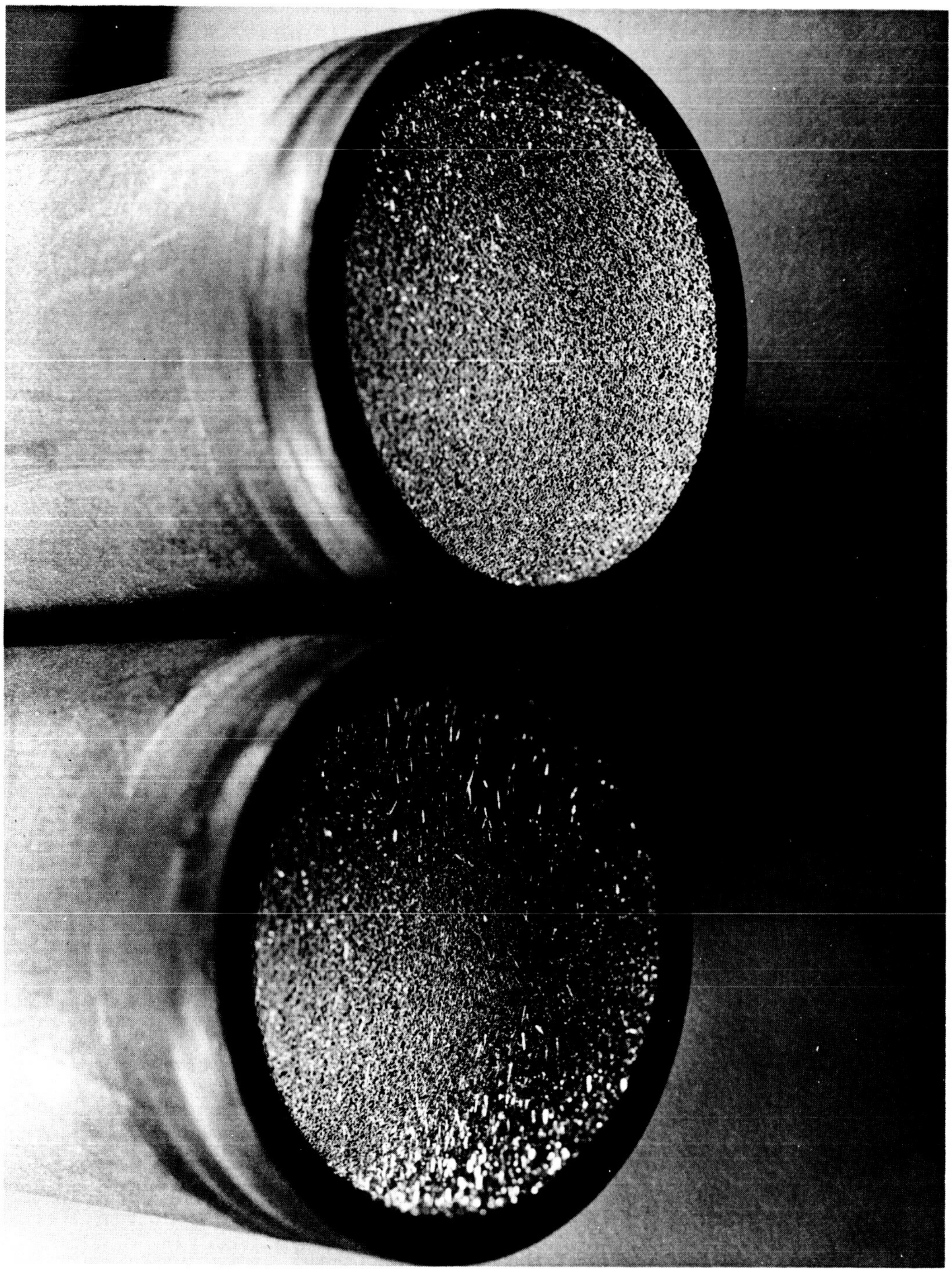


Figure 1. Photograph Showing the Effect of Vanadium on the Growth of B_4C Whiskers. Of The Two Growth Tubes Shown, Vanadium was Added to the Charge Only in the Furnace Containing the Lower Tube.

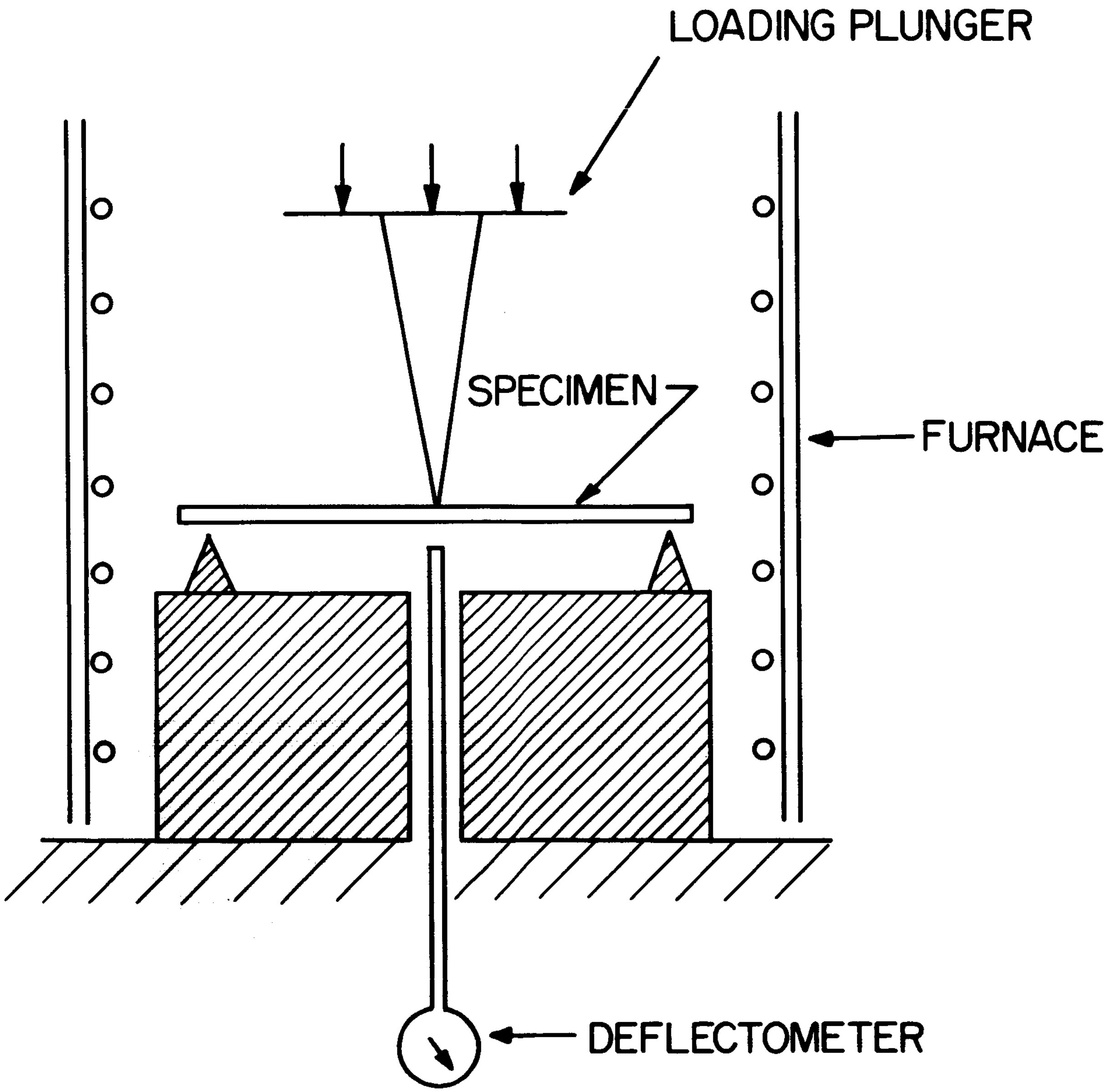
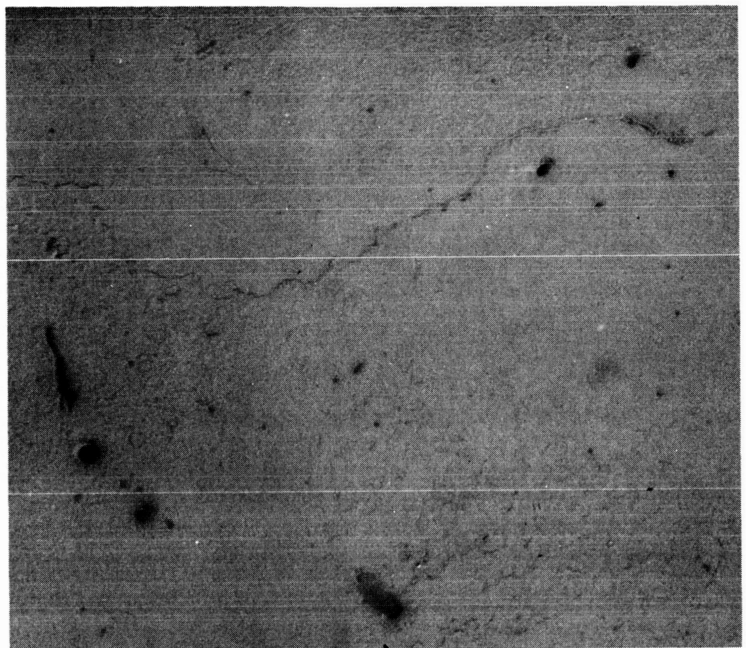
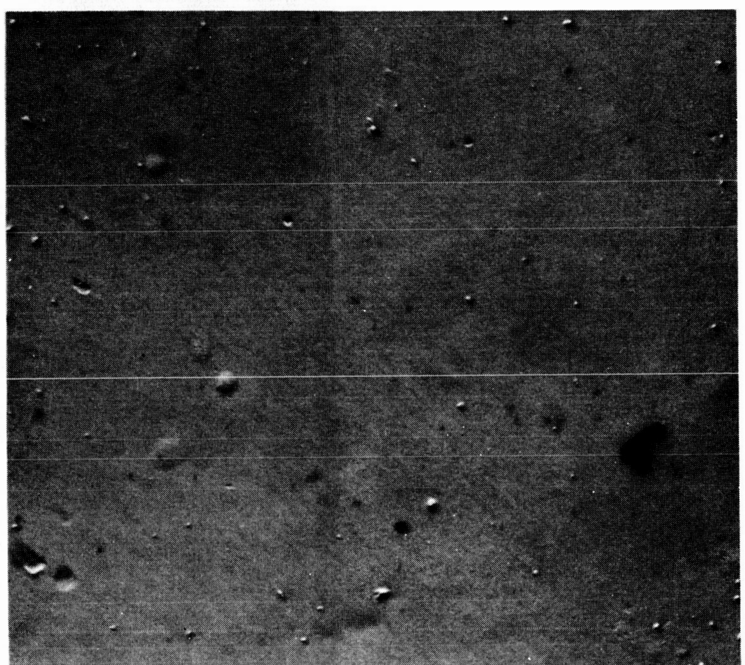


Figure 2. Proposed Schematic Diagram of System for Testing of B_4C Whiskers at Elevated Temperatures.



(a)



(b)

Figure 3. Electron Photomicrographs at 7500X of Smooth B_4C Whiskers

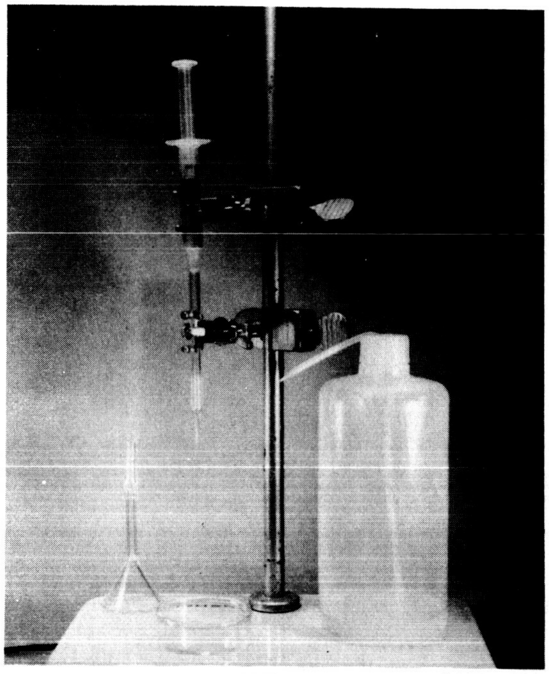


Figure 4. Photograph at 1/3 Size of Tube-Capillary and Arrangement for Expoxy Impregnation of B_4C Whisker Bundles.

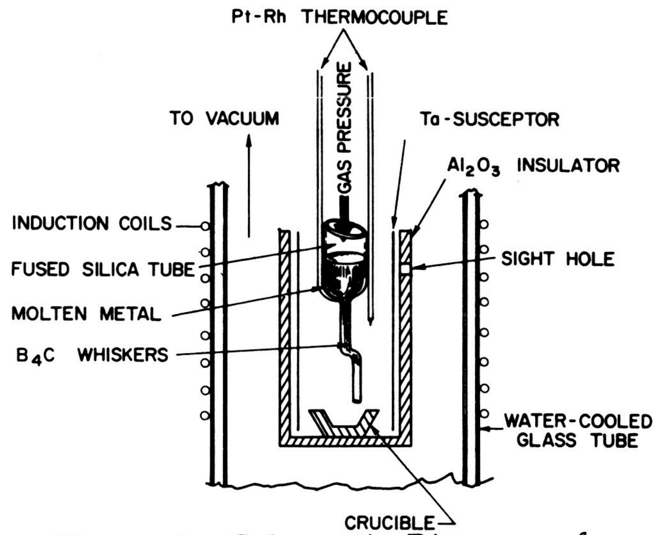


Figure 5. Schematic Diagram of Furnace for Fabricating B_4C-Metal Composites by Pneumatic Pressure Technique.

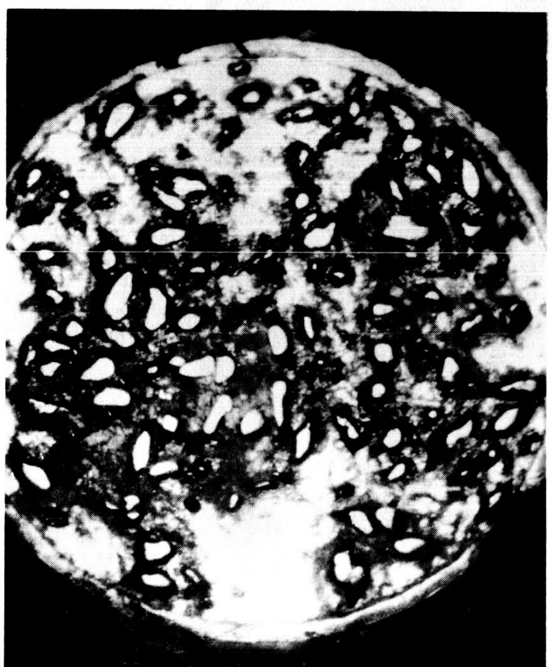


Figure 6. Cross-Section of a Typical B_4C Aluminum Composite - 154X.